Study of the structural and electrical behavior of Bi(Mg,Ti)O₃ modified (Ba,Ca)TiO₃ ceramics

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The ability of BaTiO₃ to form solid solutions with different dopants (both iso- and aliovalent) makes it versatile for various applications. In the present study, (Ba,Ca)TiO₃ (BCT) is modified with Bi(MgTi)O₃ (BMT) in search for new lead-free ferroelectric material and improve their properties. For this purpose, BCT acts as a main base material and BMT acts as a modifier to fabricate a multifunctional material. In this study, we report the structural and electrical properties of lead free piezo-ceramics (1 - x) (Ba_{0.8}Ca_{0.2})TiO₃-xBi(Mg_{0.5}Ti_{0.5})O₃ with x = 0.2, 0.4, 0.5 prepared by solid-state sintering technique. Single perovskite phase with tetragonal structure is obtained for all the compositions, which is reconfirmed by the Raman Spectroscopic study. Dielectric study confirm the temperature stable behavior of the dielectric permittivity values above 300°C. The dielectric constant value decreases with increase in BMT doping content. Impedance Spectroscopic study confirms non-Debye type dielectric relaxation in the specimen. The Nyquist plot and conductivity studies show the negative temperature coefficient of resistance behavior (NTCR) of the samples.

Keywords: Perovskite; Raman analysis; non-Debye type; XRD; ferroelectrics.

1. Introduction

Pb(ZrTi)O₃-based ceramics contain up to 60 wt.% of lead,¹ which has impacts on the human health and the environment. The high toxicity of PbO and high vapor pressure during high temperature processing have stimulated an increasing demand for environment-friendly materials. Research on lead-free piezoelectric and/or ferroelectric materials is mainly focused on barium titanates, alkali niobates and modified bismuth titanates.^{2,3} These materials play an important role for electronic devices such as actuators, sensors, accelerators, ultrasonic motors, transducers, filters, resonators and micro electromechanical systems (MEMS). Barium titanate (BaTiO₃) is an ABO₃ perovskite-type structure; where barium occupies the A-site and titanium occupies the B-site which slightly deviate from the center. Due to this structure barium titanate exhibits excellent piezoelectric, ferroelectric and electrical properties such as high dielectric constant with low dielectric loss and is widely used as capacitors and ferroelectric memory units.^{4,5} BaTiO₃ undergoes five different phase transitions known as the polymorphic phase transitions (PPT), namely; hexagonal (>1733 K), cubic (Paraelectric) (>393 K up to 1733 K), tetragonal (>278 K up to 393 K), orthorhombic (> -363 K up to 278 K) and rhombohedral (below -363 K).⁶⁻⁸ The dielectric properties of barium titanate can be modified and/or improved by the addition of

the dopants such as La³⁺, Ca²⁺, Mn⁴⁺, Nb⁵⁺ and Zr⁴⁺ to occupy Ba²⁺ on A sites or Ti⁴⁺ on B sites of the solid solution.⁹⁻¹¹ Among them Ca-doped BaTiO₃ (BCT) is considered to be one of the foremost potential candidates for the lead-free electro-optic modulators and memory devices. The substitution of Ca ions at A-site is an effective way of stabilizing the tetragonal phase of BaTiO₃ at low temperatures. Moreover, as Ca²⁺ ions is smaller than Ba²⁺ ion they form additional polarization components as compared to Ti-O distortion.¹² By the doping of Ca²⁺ ion; temperature dependency and reliability of dielectric property of the barium titanate are improved.^{13,14} (Ba, Ca)TiO₃ is used in different applications such as capacitor materials (including multilayer ceramic capacitors), dielectric filters, dielectric resonators, dielectric antennas and phase shifters. (Ba, Ca)TiO₃ crystals are used in advanced laser systems, optical storage devices, optical interconnects and photo-refractive applications.¹⁵ (Ba_{0.70}Ca_{0.30})TiO₃ (BCT) shows high energy density with good energy storage efficiency (58% before ageing, 61% after ageing) suggesting BCT as a strong candidate for high energy density capacitor applications.¹⁶

Bi-based perovskite, Bi(Mg_{1/2}Ti_{1/2})O₃-PbTiO₃ (BMT-PT) exhibits a high Curie temperature with an enhanced tetragonality synthesized by solid-state reaction method.¹⁷ (1 - x)Bi(Mg_{1/2}Ti_{1/2})-xPbTiO₃ ceramics exhibit relatively

high Curie temperature ($\sim 430^\circ\text{C}$) and good piezoelectric properties ($d_{33} \sim 200\text{pC/N}$) around morphotropic phase boundary (MPB) as compared to pure PbTiO_3 .¹⁷ For $(1-x)\{0.62\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3-0.38\text{PbTiO}_3\}-x\text{LiNbO}_3$ ceramics, dielectric permittivity around 1300–3800 with low dielectric losses and high remnant polarization were obtained in the temperature range $100\text{--}400^\circ\text{C}$ for $0.02 \leq x \leq 0.06$ samples.^{18,19} These materials also show high transition temperature but due to high electrical conductivity the piezoelectric and dielectric properties were limited. Through systematic research, a number of MPB systems based on $\text{Bi}(\text{M})\text{O}_3\text{--PbTiO}_3$ ($\text{M} = \text{Ti}^{4+}, \text{Sc}^{3+}, \text{Zn}^{2+}, \text{Nb}^{5+}$) have been explored by different researchers. Single-phase BMT–PT is reported in bulk form with high density $>95\%$ and grain sizes in μm range ($1.5\text{--}2\mu\text{m}$) and also the crystal structure transformed from rhombohedral to tetragonal system with increasing temperature.²⁰

Ca modified BaTiO_3 and $\text{Bi}(\text{Mg}, \text{Ti})\text{O}_3$ exhibits a high degree of stability at elevated temperatures, superior to unmodified $\text{BaTiO}_3\text{--Bi}(\text{Mg}, \text{Ti})\text{O}_3$ dielectric in terms of stability in relative permittivity and operating temperature range.²¹ The purpose of this study is to investigate with a special emphasis on the influence of $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ doping on the structural, dielectric and electrical properties of $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3$ ceramic system by using the X-ray diffraction technique, Raman spectroscopy and impedance spectroscopy.

2. Experimental Procedure

In this experiment, $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3\text{--}x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramic were prepared by

solid-state method using analytical grade reagents with more than 99% purity from Sigma Aldrich. CaCO_3 , BaCO_3 , TiO_2 , MgO , Bi_2O_3 were used as the starting materials. The chemicals were all weighed according to the stoichiometric calculations and the weighed chemicals were mixed with 2-propanol and ball milled for 72 h using zirconia balls as the milling media. The powders so obtained were dried overnight and calcined at 900°C for 3 h. The calcined powders were grinded to obtain fine powder, which was cold pressed into cylindrical disks of 10 mm diameter and 1 mm thickness. PVA (10% mol. wt.) was added as the binder and sintered at temperature 1200°C for 3 h. Silver paste was used as electrodes on both sides and heated at 500°C for 30 min. X-ray diffractometer (XRD) (Bruker D8 Advance) with $\text{CuK}\alpha 1$ radiation ($\lambda = 1.5406\text{ \AA}$) was employed for the identification of crystal structure. Room temperature Raman Spectra was performed on Micro Raman system from Jobin Horiba LABRAM-HR from 150 to 1000 cm^{-1} range. Dielectric constant, loss tangent and impedance parameters were measured using PSM1735 Impedance Analyzer in a frequency range of 100 Hz to 1 MHz from room temperature up to 500°C with the samples being heated in Carbolite (MTF9/15/130) tube furnace.

3. Results and Discussion

Figure 1 shows the room temperature X-ray diffraction pattern of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3\text{--}x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4, 0.5$) ceramic system at room temperature. All patterns showed that the samples have a single phase with

Fig. 1. Room temperature XRD patterns of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3\text{--}x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics.

a tetragonal structure. All the reflection peaks were indexed using observed inter-planar spacing d , and the lattice parameters of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ were determined by using least-squares refinement method. The tetragonality decreases with increasing doping of Bi $(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ in BaTiO_3 matrix. The diffraction peaks shift slightly towards the lower angle side with increase in the doping of $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$. This may be due to the difference in the ionic radii of the various B-site ions. All the reflection peaks in XRD pattern were used for estimation of the average particle size using the Debye–Scherrer equation²²

$$t = \frac{0.9\lambda}{B \cos \theta_B}, \quad (1)$$

$$B = (B_M^2 - B_S^2)^{1/2}, \quad (2)$$

where t is the diameter of the particle, λ is the X-ray wavelength (0.154 nm), B_M and B_S are the measured peak broadening and instrumental broadening in radian, respectively, and θ_B is the Bragg angle of the reflection. The calculated average particle size from Eq. (1) is about 40 nm.

Figures 2(a)–2(c) show SEM images of the samples of the fractured surface of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramic systems at room temperature for $x = 0.2, 0.4$ and 0.5 , respectively. A little amount of porosity was observed in $x = 0.2$, for $x = 0.4$ and 0.5 , mixed intergranular and transgranular fracture phenomena is present in the compositions, which shows that more $x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ substitution may lower the sintering temperature. The fine-grained material with an average grain size range from 2 to $7\ \mu\text{m}$ for all the compounds.

Figures 3(a)–3(c) show the Raman spectra of $\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3\text{--Bi}(\text{Mg}_{0.5}, \text{Ti}_{0.5})\text{O}_3$ ceramics as a function of wave number at room temperature where $x = 0.2, 0.4, 0.5$, respectively. The modes at $515\text{--}520\text{ cm}^{-1}$ A_1 (TO) and 739 cm^{-1} A_1 (LO) represents transverse optic mode of Ti–O stretching vibrations in TiO_6 octahedra and its longitudinal pairs, respectively. The band at $298\text{--}310\text{ cm}^{-1}$ represents mixed B_1+E (TO) originating from Ti–O torsional vibrations.²³ In low frequency range 246 cm^{-1} is assigned to hard mode B_{1g} as a result of rotation of the oxygen octahedron cage. The peak at 198 cm^{-1} may be assigned to fundamental TO mode of A_1 symmetry.

Figure 4(a) shows the variation of dielectric constant (ϵ') and loss tangent ($\tan \delta$) with temperature at frequency 10 kHz of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics. As in normal ferroelectrics, the dielectric constant of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramics with $x = 0.2, 0.4$ and 0.5 increases gradually with increasing temperature up to the transition temperature and thereafter it decreases with increasing temperature. The peak value of dielectric constant decreases with increase in x and $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ with $x = 0.2$ shows the maximum value of dielectric constant. Also the dielectric constant temperature curve flattens i.e., diffusivity

Fig. 2. (a–c) SEM micrographs of surface of the $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics.

increases with increasing frequency. The most prominent feature of the curve is the temperature stability of the dielectric permittivity after 300°C . The broadening in the dielectric peaks is a common feature in solid solutions. The occurrence of diffuse phase transition in BMT–BT may be due to the presence of more than one cations in sub-lattice which may produce heterogeneity. Figure 4(b) shows the variation of dissipation factor ($\tan \delta$) as a function of temperature of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramics at frequency 10 kHz. Loss tangent increases with increasing temperature and decreasing frequency. An important contribution to the losses may occur in bulk ceramics by the defects associated with the grain boundaries. At high temperatures and low frequencies, all the different types of polarization

Fig. 3. (a–c) Room temperature (300 K) Raman spectra of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics as function of wave number ranges from 50 to 900 cm^{-1} as function of x .

contribution to the dielectric loss is high. The value of dielectric loss decreases with increase in doping, the loss tangent value reduces by almost 50% for $x = 0.2$ to $x = 0.5$.

The electrical properties of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4, 0.5$) ceramic were investigated by a complex impedance spectroscopy (CIS) technique. It is an important tool to analyze the electrical properties of a polycrystalline material in view of its capability of correlating the electrical behavior of the sample to its microstructure. The use of function Z^* is particularly appropriate for the resistive and/or conductive analysis where the long-range conduction dominates, whereas the ϵ^* and M^* functions are suitable when localized relaxation dominates. So the plotting of ac data in terms of impedance, electric modulus and dielectric permittivity simultaneously provides a

complete understanding of all the physical processes taking place in the material.

Figures 5(a)–5(c) show the temperature-dependent spectra (Nyquist plot) of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4, 0.5$) ceramics. The impedance spectra are characterized by the appearance of a single semicircle arc and the intercept of the semicircle arc with the real axis (Z') gives us an estimate of the bulk resistance (R_b) of the material. It is clear from the figure that semicircle arcs becomes smaller with the increasing temperature. This means that bulk resistance of the material decreases with increasing temperature showing a typical semiconducting property, i.e., negative temperature coefficient of resistance (NTCR) behavior. It is observed that in all the samples with increasing temperature the slope of the curve lines decreases and the curves

Fig. 4. (a-b) Variation of dielectric constant (ϵ) and loss tangent ($\tan \delta$) of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics with temperature at frequency 10 kHz.

Fig. 5. (a-c) Nyquist plot of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) Ceramics at different temperatures.

bend towards real (Z') axis above 300°C; a semicircle could be traced, indicating the increase in conductivity of the samples. It can also be observed that the peak maxima of the plots decrease and the frequency for the maximum shifts to higher values with the increase in temperature. It can be noticed that the complex impedance plots are not represented by full semicircle, rather the semicircle arc is depressed and the center of the arc lies below the real (Z') axis suggesting the relaxation to be poly-dispersive non-Debye type. This may be due to the presence of distributed elements in the material electrode system.

Figures 6(a)–6(c) show the variation of real part of impedance (Z') as a function of frequency at different temperatures of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics. The pattern shows a sigmoid variation as a function of frequency in the low frequency region followed by a saturation region in the high

frequency region. This suggests the presence of mixed nature of polarization behavior in the material, such as electronic, dipolar and orientation polarization. A decreasing trend of Z' with rise in temperature suggests the presence of NTCR in the material in the low frequency region but tends to merge in the high frequency region at almost all temperatures. These results indicate a possibility of increase in ac conductivity with rise in temperature in the high frequency region which is due to the release of space charge and lowering in the barrier properties of the material.

Figures 7(a)–7(c) present the variation of imaginary part of impedance (Z'') as a function of frequency at different set of temperatures. For $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ $x = 0.2$ ceramic, with increasing frequency, the imaginary part of impedance (Z'') increases and then decreases after a particular point. The value of frequency of this point is known as relaxation frequency. At higher frequency side all the

Fig. 6. (a–c) Variation of real part (Z') of impedance with frequency at different temperatures of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics.

Fig. 7. (a–c) Variation of imaginary part (Z'') of impedance with frequency at different temperatures of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics.

Fig. 8. Impedance scaling behavior of compounds in the master curves of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics.

Fig. 8. (Continued)

curves are merged. As the temperature increases, the peak in Z'' versus frequency plot becomes more prominent. The peak shifts towards higher frequency side with increasing temperature indicating the decrease of the bulk resistance of the material. Also, the magnitude of Z'' decreases with increasing temperature implying that dielectric relaxation is temperature dependent, for $x = 0.2$ and is apparently not a single relaxation time. Whereas for $x = 0.4$ and 0.5 $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramics value of imaginary part of impedance (Z'') decreases with increasing frequency.

Figures 8(a)–8(c) show the normalized plot of $Z''/Z''_{\max}$ versus $\log(f/f_{\max})$ at different temperatures for different compositions of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramics. The normalized plot overlaps on a single master curve at different temperatures i.e., same shape and pattern in the peak position with slight variation in full width at half maximum (FWHM) with rise in temperature. This master curve confirms the evidence of the temperature-independent conduction transport mechanism. It is also observed from the figure that the $Z''/Z''_{\max}$ curves are not symmetric, implying a nonexponential behavior of the conductivity relaxation. The FWHM of $Z''/Z''_{\max}$ versus $\log(f/f_{\max})$ is wider than the width of a Debye peak, which shows the presence of non-Debye type of relaxation phenomenon.²³

4. Conclusions

Perovskite structured $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ (where $x = 0.2, 0.4$ and 0.5) ceramic was prepared using high temperature solid-state reaction route. Room temperature XRD study suggests that the composition has a single-phase tetragonal symmetry. The diffraction peaks shift slightly towards a lower angle side as we increase the doping concentration of $\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$. As in normal

ferroelectrics, the dielectric constant of $(1-x)\text{Ba}_{0.8}\text{Ca}_{0.2}\text{TiO}_3-x\text{Bi}(\text{Mg}_{0.5}\text{Ti}_{0.5})\text{O}_3$ ceramics with $x = 0.2, 0.4$ and 0.5 increases gradually with increasing temperature up to the transition temperature and thereafter it decreases with increasing temperature. Impedance spectroscopy shows the presence of single semicircle arc at all reported temperatures which indicates that there is a presence of grain interior (bulk) property in material. All samples showed dielectric relaxation, which is found to be of non-Debye type and the relaxation frequency shifted to higher side with the increase of temperature. The Nyquist plot and conductivity studies showed the NTCR behavior of the samples.

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